PCT/EP 03 / 05456

INVESTOR IN PEOPLE

EPO - DG 1

28 05. 2003

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REC'D 11 JUL 2003

WIPO PCT

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

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17 JUN 2002

The Patent Office
Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

MBZ-0488

17JUN02 E726113-1 D03051
P01/7700 0.00-0213765.1

2. Patent application number
(The Patent Office will fill in this part)

0213765.1

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

MBT HOLDING AG
Vulkanstrasse 110
CH-8048 Zürich
Switzerland

Patents ADP number *(if you know it)*

7171101001

If the applicant is a corporate body, give the country/state of its incorporation

Switzerland

4. Title of the invention

ADMIXTURE

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Mr. P. Brown
FEB MBT
Albany House
Swinton Hall Road
Swinton
MANCHESTER M27 4DT

Patents ADP number *(if you know it)*

7235385001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

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Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	1
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature [signature] Date: 17.06.02

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr. P. Brown, FEB MBT
(0161) 794 74 11

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DUPLICATE

ADMIXTURE

This invention relates to low alkali and alkali-free accelerators for sprayed cementitious compositions.

The use in cementitious compositions such as concrete to be applied by spraying of low alkali and alkali-free accelerators in place of the traditional aluminates and other strongly alkaline materials is now well established. The major components of such accelerators are aluminium compounds, the most commonly encountered being aluminium sulphate and amorphous aluminium hydroxide. In addition to these aluminium compounds, a variety of other components have been used in such accelerators, these including alkanolamines, other aluminium salts (such as oxalates and nitrates) and various organic acids. More recent compositions have involved the use of fluoride ions.

The major problem in the art is to find an accelerator composition that combines acceptable performance, acceptable stability and an acceptable compressive strength. Stability can be a problem, especially in the more extreme conditions sometimes encountered in tunnels, and a reasonable shelf-life is necessary for a practical accelerator. All accelerators used in spraying concrete lower the compressive strength compared to the compressive strength of the same concrete without accelerator. It is necessary that this lowering be kept to a minimum. In addition, a good early strength development in the 1-4 hour period after spraying is particularly desired.

In addition, the worldwide variation in cement types causes problems. What works well with one cement in, say, Europe will not necessarily work so well with an Australian cement. It is difficult to formulate an accelerator that will work acceptably well with all types. Particularly difficult are Japanese ordinary Portland cements (OPCs).

It has now been found that a particular combination of materials gives an accelerator that performs especially well and is very stable. The invention therefore provides an accelerator composition adapted to be used with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3:

Component 1 - aluminium sulphate

Component 2 – at least one of an alkanolamine and an alkylene diamine

Component 3 - hydrofluoric acid

optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present: optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present:

Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, sodium sulphate, potassium sulphate and lithium sulphate;

Component 5 - $C_1 - C_{10}$ aliphatic mono- and dicarboxylic acids and their metal salts;

Component 6 - amorphous aluminium hydroxide;

Component 7 - phosphoric acid

the ingredients being present in the following proportions (active ingredients by weight);

Component 1 - from 30 to 60%, calculated on the basis of 17% aluminium sulphate;

Component 2 - from 0.1 to 15%

Component 3 - from 0.2 to 8.0%

Component 4 - up to 15%

Component 5 - up to 15%

Component 6 - up to 15%

Component 7 - up to 3%.

Component 1, aluminium sulphate, may be any aluminium sulphate used in the manufacture of accelerators. It may be fully hydrated, or totally or partially calcined. A typical grade, and the one on which the proportion is based, is "17%" aluminium sulphate ($Al_2(SO_4)_3.14H_2O$) (called thus because that is the proportion of aluminium oxide therein), should any other aluminium sulphate be required, he appropriate quantity can be easily calculated on this basis. Preferably Component 1 is present in the proportion of from 42-56% by weight of the total accelerator composition.

Component 2, alkanolamine or alkyldiamine, may be any alkanolamine or alkylene diamine, but is preferably ethylene diamine, diethanolamine or triethanolamine, most preferably diethanolamine. It is preferably present in the proportion of from 0.1- 10%, more preferably from 0.1 –8%, by weight of the total accelerator composition. It is possible to use a combination of two or more of such materials.

Component 3, hydrofluoric acid is generally used as an aqueous solution of about 40% HF by weight. The proportion of hydrofluoric acid present in the total accelerator composition (as HF) is preferably from 4-6% by weight of the total accelerator.

Component 4 may be selected from among the materials previously named. Although sodium and potassium are alkali metals, the proportion of such metals in the accelerator compositions according to this invention are sufficiently low to permit these accelerators to be considered as alkali-free according to the accepted European definition (lower than 1% (weight) of Na_2O equivalent). Up to 8.5% Na_2O equivalent is considered "low alkali" and is acceptable for many purposes – in many cases, rigorous exclusion of alkali on health and environmental grounds is not necessary and a small proportion of at least one alkali metal enhances the early strength development. Thus, for the purposes of this invention, and contrary to the current practices of the art with respect to alkali-free accelerators, it is preferred that a minor proportion of alkali metal be present. This proportion is preferably no higher than 5% Na_2O equivalent. The preferred proportion of Component 4 is from 1-10% by weight of the total accelerator composition. Component 4 is typically added to the accelerator composition as a 30% weight solution in water.

Component 5 may be selected from one or more of the group of acids. Especially preferred are formic, oxalic and glycolic acids and their metal salts, but other acids, such as acetic, propionic, succinic, citric and tartaric acids are also useful. Preferred proportions of Component 5 are from 2 - 10%, more preferably from 4 - 8%, by weight of the total accelerator composition.

It is required that at least one of Component 4 and Component 5 be present in the composition. The preferred Components 4 and/or 5 for the purposes of this invention are

sodium oxalate, potassium oxalate and mixtures of one or both of these with lithium hydroxide. The LiOH/sodium-potassium oxalate mixtures are particularly preferred.

Component 6, aluminium hydroxide, is amorphous aluminium hydroxide of the type normally used in accelerators for sprayed concrete. It is preferably present in the proportion of up to 10% by weight of the total accelerator composition.

Component 7, phosphoric acid, acts as a stabiliser. Although it is possible to omit it, it confers a useful degree of stability on the accelerator compositions of this invention, a vital consideration in tunnelling operations where the accelerator may have to remain in a ready-to-use state for long periods. It is therefore preferably present, and in a concentration of from 0.1- 2% by weight of the accelerator composition.

The accelerator compositions may be prepared by simply mixing the abovementioned components in any order and stirring to give an aqueous solution. In some cases, additional water will need to be added. The final composition will generally comprise from 40-70% by weight of water.

Given the nature of the ingredients, the resulting accelerator composition will not be a simple mixture of ingredients but a complex blend of reaction products. For example, the HF will react with some other components (most especially aluminium hydroxide, if any be present). This composition is very stable, having a shelf life under normal storage conditions of several months.

In use, the accelerator composition of the invention is injected at a spray nozzle in the conventional manner. The dose is typically from 5 – 12% by weight accelerator composition based on cement weight. The invention also provides a method of applying a cementitious composition to a substrate by spraying, comprising the steps of mixing a batch of fluid cementitious composition and conveying it to a spray nozzle, there being injected at the nozzle an accelerator as hereinabove described.

Sprayed cementitious compositions that utilise accelerator compositions according to this invention exhibit an unusually rapid build-up of compressive strength. In addition, the

accelerator compositions work well with an unusually wide variety of cements, including Japanese cements, with which other alkali-free accelerators give less satisfactory results. The invention also provides a hardened cementitious layer applied to a substrate by spraying through a spray nozzle, there having been added at the nozzle an accelerator as hereinabove described.

The invention is further illustrated by the following non-limiting examples in which all parts are by weight.

A number of accelerators are added to a test mortar mix having the following constitution:

water	198 parts
ordinary Portland cement	450 "
sand (DIN 196-1)	1350 "
superplasticiser	2.7 "

The cement is Tayheiuo OPC, a commonly-used Japanese cement. The superplasticiser used is NT-1000 ex NMB Ltd., Japan.

Example 1

To the abovementioned mix is added with thorough mixing 31.5 parts of an accelerator according to the invention and having the following composition (given as percentages by weight):

aluminium sulphate ($16H_2O$)	35
diethanolamine	2.1
sodium sulphate	11.2
oxalic acid	7.5
hydrofluoric acid	6
amorphous aluminium hydroxide	9.5
water	to 100%

Example 2

Example 1 is repeated, with the exception that the 31.5 parts of the accelerator according to the invention is replaced by a commercially-available alkali-free accelerator sold as MEYCO® SA162.

Example 3

Example 1 is repeated, with the exception that the 31.5 parts of the accelerator according to the invention is replaced by a commercially-available alkali-free accelerator sold as MEYCO® SA170.

The samples are tested for compressive strength according to prEN (preliminary European Standard) 12394 and the results obtained are shown below:

Example No.	Compressive strength (MPa) at		
	6h	1d	7d
1	3.6	20.1	39
2	1.4	1.8	23.2
3	0.8	8.6	28.9

It can be seen that the composition comprising the accelerator according to the invention develops compressive strength earlier than the compositions comprising the commercial accelerators, and that the final strength is substantially higher.

CLAIMS:

1. An accelerator composition adapted to be used with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3:

Component 1 - aluminium sulphate
Component 2 – at least one of an alkanolamine and an alkylene diamine
Component 3 - hydrofluoric acid

optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present:

Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, sodium sulphate, potassium sulphate and lithium sulphate;
Component 5 - C_1 – C_{10} aliphatic mono- and dicarboxylic acids and their metal salts;
Component 6 - amorphous aluminium hydroxide;
Component 7 - phosphoric acid

the ingredients being present in the following proportions (active ingredients by weight);

Component 1 - from 30 to 60%, calculated on the basis of 17% aluminium sulphate;
Component 2 - from 0.1 to 15%
Component 3 - from 0.2 to 8.0%
Component 4 - up to 15%
Component 5 - up to 15%
Component 6 - up to 15%
Component 7 - up to 3%.

2. An accelerator according to claim 1, in which Component 4 is present.

3. An accelerator according to claim 2, in which Component 4 contains alkali metal and is present to the extent that the alkali metal content is a maximum of 8.5% Na_2O equivalent

4. A method of applying a cementitious composition to a substrate by spraying, comprising the steps of mixing a batch of fluid cementitious composition and conveying it to a spray nozzle, there being injected at the nozzle an accelerator according to claim 1.

5. A hardened cementitious layer applied to a substrate by spraying through a spray nozzle, there having been added at the nozzle an accelerator according to claim 1.

ABSTRACT

An accelerator composition for use with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3

Component 1 - aluminium sulphate
Component 2 – at least one of an alkanolamine and an alkylene diamine
Component 3 - hydrofluoric acid

optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present:

Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, sodium sulphate, potassium sulphate and lithium sulphate;
Component 5 - $C_1 - C_{10}$ aliphatic mono- and dicarboxylic acids and their metal salts;
Component 6 - amorphous aluminium hydroxide;
Component 7 - phosphoric acid.

The accelerators have excellent long-term stability and work werll with "difficult" cements, such as some Japanese OPCs.

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28 05. 2003

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The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

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Signed

Dated 14 May 2003

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The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

MBZ-0514

25FEB03 E787426-1 D03051
P01/7700 0.00-0304158.9

2. Patent application number
(The Patent Office will fill in this part)

0304158.9

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

MBT Holding AG
Vulkanstrasse 110
CH-8048 Zürich
Switzerland

25 FEB 2003

Patents ADP number *(if you know it)*

717110 1001

If the applicant is a corporate body, give the country/state of its incorporation

Switzerland

4. Title of the invention

ADMIXTURE

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Mr. P. Brown
FEB MBT
Albany House
Swinton Hall Road
Swinton
MANCHESTER M27 4DT

7235385001

Patents ADP number *(if you know it)*

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

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b) there is an inventor who is not named as an applicant, or

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Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
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Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature

Date 25.02.2003

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr. P. Brown, FEB MBT
(0161) 794 7411

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ADMIXTURE

This invention relates to low alkali and alkali-free accelerators for sprayed cementitious compositions.

The use in cementitious compositions such as concrete to be applied by spraying of low alkali and alkali-free accelerators in place of the traditional aluminates and other strongly alkaline materials is now well established. The major components of such accelerators are aluminium compounds, the most commonly encountered being aluminium sulphate and amorphous aluminium hydroxide. In addition to these aluminium compounds, a variety of other components have been used in such accelerators, these including alkanolamines, other aluminium salts (such as oxalates and nitrates) and various organic acids. More recent compositions have involved the use of fluoride ions.

The major problem in the art is to find an accelerator composition that combines acceptable performance, acceptable stability and an acceptable compressive strength. Stability can be a problem, especially in the more extreme conditions sometimes encountered in tunnels, and a reasonable shelf-life is necessary for a practical accelerator. All accelerators used in spraying concrete lower the compressive strength compared to the compressive strength of the same concrete without accelerator. It is necessary that this lowering be kept to a minimum. In addition, a good early strength development in the 1-4 hour period after spraying is particularly desired.

In addition, the worldwide variation in cement types causes problems. What works well with one cement in, say, Europe will not necessarily work so well with an Australian or a Japanese cement. It is difficult to formulate an accelerator that will work acceptably well with all types.

It has now been found that a particular combination of materials gives an accelerator that performs especially well and is very stable. The invention therefore provides an accelerator composition adapted to be used with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3:

Component 1 - aluminium sulphate

Component 2 – at least one of an alkanolamine and an alkylene diamine or triamine

Component 3 - hydrofluoric acid

optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present;

Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, magnesium carbonate, sodium sulphate, potassium sulphate, magnesium sulphate and lithium sulphate;

Component 5 - $C_1 - C_{10}$ aliphatic mono- and dicarboxylic acids and their metal salts;

Component 6 - aluminium hydroxide;

Component 7 - at least one of phosphoric acid and phosphorous acid

the ingredients being present in the following proportions (active ingredients by weight):

Component 1 - from 30 to 60%, calculated on the basis of 17% aluminium sulphate;

Component 2 - from 0.1 to 15%

Component 3 - from 0.2 to 8.0%

Component 4 - up to 15%

Component 5 - up to 15%

Component 6 - up to 15%

Component 7 - up to 5%.

Component 1, aluminium sulphate, may be any aluminium sulphate used in the manufacture of accelerators. It may be fully hydrated, or totally or partially calcined. A typical grade, and the one on which the proportion is based, is "17%" aluminium sulphate ($Al_2(SO_4)_3.14.3H_2O$) (called thus because that is the proportion of aluminium oxide therein). should any other aluminium sulphate be required, he appropriate quantity can be easily calculated on this basis. Preferably Component 1 is present in the proportion of from 30-46% by weight of the total accelerator composition.

Component 2, alkanolamine, alkylene diamine and alkylene triamine may be any such material, but is preferably ethylene diamine, ethylene triamine, diethanolamine or triethanolamine, most preferably diethanolamine. It is preferably present in the proportion of from 0.1- 10%, more preferably from 0.1 –8%, by weight of the total accelerator composition. It is possible to use a combination of two or more of such materials.

Component 3, hydrofluoric acid is generally used as an aqueous solution of about 40% HF by weight. The proportion of hydrofluoric acid present in the total accelerator composition (as HF) is preferably from 2-4% by weight of the total accelerator.

Component 4 may be selected from among the materials previously named. Although sodium and potassium are alkali metals, the proportion of such metals in the accelerator compositions according to this invention may be sufficiently low to permit these accelerators to be considered as alkali-free according to the accepted European definition (lower than 1% (weight) of Na_2O equivalent). Up to 8.5% Na_2O equivalent is considered "low alkali" and is acceptable for many purposes – in many cases, rigorous exclusion of alkali on health and environmental grounds is not necessary and a small proportion of at least one alkali metal enhances the early strength development. Thus, for the purposes of this invention, and contrary to the current practices of the art with respect to alkali-free accelerators, it is preferred that a minor proportion of alkali metal be present. This proportion is preferably no higher than 5% Na_2O equivalent. The preferred proportion of Component 4 is from 1-10% by weight of the total accelerator composition. Component 4 is typically added to the accelerator composition as a 30% weight solution in water.

Component 5 may be selected from one or more of the group of acids. Especially preferred are formic, oxalic and glycolic acids and their metal salts, but other acids, such as acetic, propionic, succinic, citric and tartaric acids are also useful. Preferred proportions of Component 5 are from 2 - 10%, more preferably from 4 - 8%, by weight of the total accelerator composition.

It is required that at least one of Component 4 and Component 5 be present in the composition. The preferred Components 4 and/or 5 for the purposes of this invention are

sodium oxalate, potassium oxalate and mixtures of one or both of these with lithium hydroxide. The LiOH/sodium-potassium oxalate mixtures are particularly preferred.

Component 6, aluminium hydroxide, is preferably amorphous aluminium hydroxide of the type normally used in accelerators for sprayed concrete. It is preferably present in the proportion of up to 10% by weight of the total accelerator composition. It is possible to use crystalline aluminium hydroxide; this is considerably cheaper, but it is difficult to dissolve and it does not perform as well as the amorphous material.

Component 7, phosphoric acid (H_3PO_4) or phosphorous acid (H_3PO_3), acts as a stabiliser. Although it is possible to omit it, it confers a useful degree of stability on the accelerator compositions of this invention, a vital consideration in tunnelling operations where the accelerator may have to remain in a ready-to-use state for long periods. It is therefore preferably present, and in a concentration of from 0.1- 2% by weight of the accelerator composition. It is possible to use a blend of both acids, but it is preferred to use phosphoric acid alone.

The accelerator compositions may be prepared by simply mixing the abovementioned components in any order and stirring to give an aqueous solution. In some cases, additional water will need to be added. The final composition will generally comprise from 40-70% by weight of water.

Given the nature of the ingredients, the resulting accelerator composition will not be a simple mixture of ingredients but a complex blend of reaction products. For example, the HF will react with some other components (most especially aluminium hydroxide, if any be present). This composition is very stable, having a shelf life under normal storage conditions of several months.

In use, the accelerator composition of the invention is injected at a spray nozzle in the conventional manner. The dose is typically from 5 – 12% by weight accelerator composition based on cement weight. The invention also provides a method of applying a cementitious composition to a substrate by spraying, comprising the steps of mixing a batch of fluid

cementitious composition and conveying it to a spray nozzle, there being injected at the nozzle an accelerator as hereinabove described.

Sprayed cementitious compositions that utilise accelerator compositions according to this invention exhibit an unusually rapid build-up of compressive strength. In addition, the accelerator compositions work well with an unusually wide variety of cements, including Japanese cements, with which other alkali-free accelerators give less satisfactory results. The invention also provides a hardened cementitious layer applied to a substrate by spraying through a spray nozzle, there having been added at the nozzle an accelerator as hereinabove described.

The invention is further illustrated by the following non-limiting examples in which all parts are by weight.

A number of accelerators are added to a test mortar mix having the following constitution:

water	198 parts
ordinary Portland cement	450 "
sand (DIN 196-1)	1350 "
superplasticiser	2.7 "

The cement is Tayheiyo OPC, a commonly-used Japanese cement. The superplasticiser used is NT-1000 ex NMB Ltd., Japan.

Example 1

To the abovementioned mix is added with thorough mixing 31.5 parts of an accelerator according to the invention and having the following composition (given as percentages by weight):

aluminium sulphate ($16H_2O$)	35
diethanolamine	2.1

sodium sulphate	11.2
oxalic acid	7.5
hydrofluoric acid	6
amorphous aluminium hydroxide	9.5
water	to 100%

Example 2

Example 1 is repeated, with the exception that the 31.5 parts of the accelerator according to the invention is replaced by a commercially-available alkali-free accelerator sold as MEYCO® SA162.

Example 3

Example 1 is repeated, with the exception that the 31.5 parts of the accelerator according to the invention is replaced by a commercially-available alkali-free accelerator sold as MEYCO® SA170.

The samples are tested for compressive strength according to prEN (preliminary European Standard) 12394 and the results obtained are shown below:

Example No.	Compressive strength (MPa) at		
	6h	1d	7d
1	3.6	20.1	39
2	1.4	1.8	23.2
3	0.8	8.6	28.9

It can be seen that the composition comprising the accelerator according to the invention develops compressive strength earlier than the compositions comprising the commercial accelerators, and that the final strength is substantially higher.

CLAIMS:

1. An accelerator composition adapted to be used with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3:

Component 1 - aluminium sulphate
Component 2- at least one of an alkanolamine and an alkylene diamine or triamine
Component 3 - hydrofluoric acid

optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present:

Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, magnesium carbonate, sodium sulphate, potassium sulphate, magnesium sulphate and lithium sulphate;
Component 5 - $C_1 - C_{10}$ aliphatic mono- and dicarboxylic acids and their metal salts;
Component 6 - aluminium hydroxide;
Component 7 - at least one of phosphoric acid and phosphorous acid.

the ingredients being present in the following proportions (active ingredients by weight);

Component 1 - from 30 to 60%, calculated on the basis of 17% aluminium sulphate;
Component 2 - from 0.1 to 15%
Component 3 - from 0.2 to 8.0%
Component 4 - up to 15%
Component 5 - up to 15%
Component 6 - up to 15%
Component 7 - up to 5%.

2. An accelerator according to claim 1, in which Component 4 is present.

3. An accelerator according to claim 2, in which Component 4 contains alkali metal and is present to the extent that the alkali metal content is a maximum of 8.5% Na_2O equivalent

4. A method of applying a cementitious composition to a substrate by spraying, comprising the steps of mixing a batch of fluid cementitious composition and conveying it to a spray nozzle, there being injected at the nozzle an accelerator according to claim 1.

5. A hardened cementitious layer applied to a substrate by spraying through a spray nozzle, there having been added at the nozzle an accelerator according to claim 1.

ABSTRACT

An accelerator composition for use with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3

Component 1 - aluminium sulphate
Component 2 – at least one of an alkanolamine and an alkylene diamine or triamine
Component 3 - hydrofluoric acid

optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present:

Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, magnesium carbonate, sodium sulphate, potassium sulphate, magnesium sulphate and lithium sulphate;
Component 5 - $C_1 - C_{10}$ aliphatic mono- and dicarboxylic acids and their metal salts;
Component 6 - aluminium hydroxide;
Component 7 - at least one of phosphoric acid and phosphorous acid.

The accelerators have excellent long-term stability and work well with "difficult" cements, such as some Japanese OPCs.